

HYDRO-GEOCHEMICAL MODELLING IN THE PASSO A CAMPALTO PHOSPHOGYPSUM DUMP IN THE LAGOON OF VENEZIA, ITALIA

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ABSTRACT

We have developed a hydrogeochemical transport model for a phosphogypsum dump located on the intertidal deposits of the Venetian Lagoon. To produce this model, we first constructed a complex conceptual and geologic model from field data, using the Groundwater Modelling System GMS™ graphical user interface. Second, we mapped the numerical MODFLOW grid onto the geological model. Third, using a FORTRAN90 code, we translated this grid into the MESH and INCON blocks that are the input files for the TOUGH2 series of codes. Finally, we ran TOUGH-REACT to model flow and reactive transport in the dump and the sediments below it. The model includes three different dump materials (phosphogypsum, bituminous, and hazardous wastes) with the pores saturated by specific [=different?] fluids. The sediments below the dump are formed by an intertidal sequence of calcareous sands and silts, in addition to clays and organic deposits, all of which are saturated with lagoon salty waters. The fluids in the dump react with the solid matrix, while the recharge from rainwater dilutes them. In turn, the percolates from the dump react with the underlying sediments and lagoon waters. In spite of the simplicity of our model, we were able to show how the pH becomes neutral at a short distance below the dump, a fact observed during water monitoring. Dissolution reactions in the dump and mineral precipitation in the sediments below suggest that the

sediments tend to contain the transport of contaminants.

INTRODUCTION

The Passo a Campalto dump is located in the Venetian Lagoon (Italy; Fig. 1 and 2). The dump is divided into two areas: the phosphogypsum section in the East and the toxic-waste section in the West.

Since the year 2000, to inhibit leaching of pollutants and infiltration in the underlying aquifers, the dump has been covered and laterally isolated by two engineered barriers, each 0.25–0.50 m thick that extend down to -10 m bsl. The internal of these two barriers, constituted by calcareous sand, was made to control the pH of percolates; the external barrier, made of clay, inhibits their outward flow. Underneath the dump, down to the depth of -10 m bls, the sequence of discontinuous interdigitated layers of clay, silty clay, silt, silty sand can be considered the lower natural barrier: as soon as the polluted water reaches larger depths, the system is assumed to be leaking. We stress that while the two engineered lateral barriers are thin and continuous, the lower barrier, while discontinuous, is more than one order of magnitude thicker than the higher.

To verify the potential reactions of the dump percolates with the lateral barriers, and those of

the underlying sediments with their formation aqueous phases, we have simulated a scenario for the geochemical evolution of this system, using the TOUGH-REACT code (Xu et al., 2005).

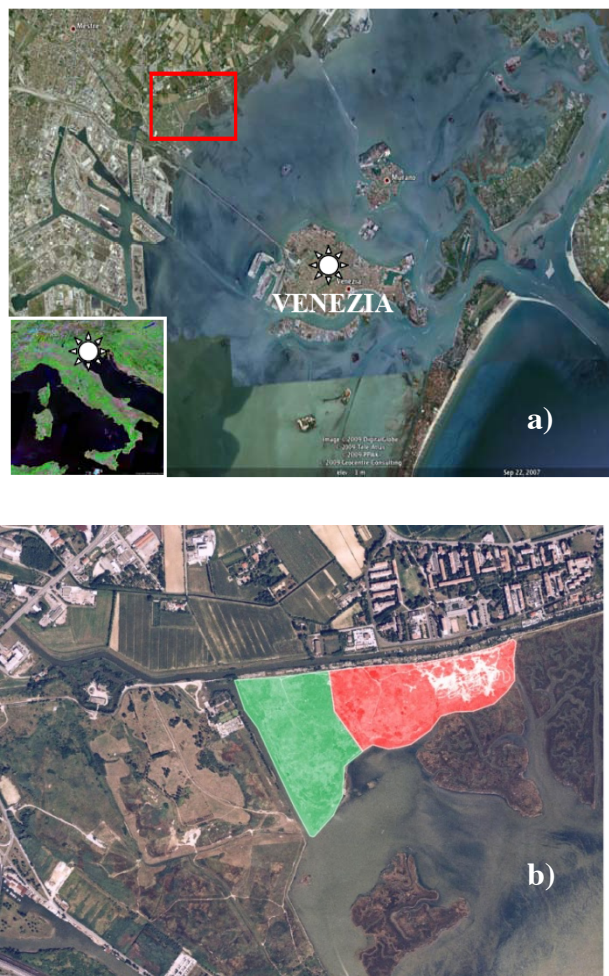
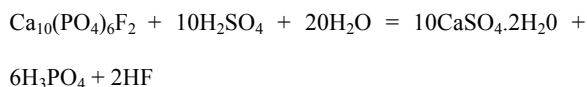


Figure 1. The Passo a Campalto dump. a) Google™ view of the Venezia Lagoon. Red box is the studied area. b) To the east are phosphogypsum (red colored), and to the west is toxic wastes (green colored).

THE DUMP

The phosphogypsum in the dump is a byproduct of the industrial processes that produce phosphates from phosphorites (Rutheford et al., 1994):



Impurities in the apatites, from which phosphogypsum is derived and which become concentrated in it, are: SiO_2 (0.1–14%), F (1.3–4.1%), CO_2 (0.2–7.3%), SO_3 (0.0–3.3%), Al_2O_3 (0.2–1.8%), Fe_2O_3 (0.1–2.6%), MgO (0.0–2.2%), and Na_2O (0.2–1.5%). Mineral impurities are quartz 10%, illite and muscovite 5%, organic matter 2%, with traces of dolomite, calcite, iron oxides, fluorite, zircon, tormaline, montmorillonite, caolinite, and pirite. The phosphogypsum itself also contains trace amounts of the anions PO_4 , OH, F, Cl, Br, and radionuclei of the ^{238}U and ^{235}Th series.

The toxic-waste dump is less well characterized, and has a few hydrocarbon waste pools both on top of it and within it.

CONCEPTUAL MODEL

Our geologic model is based on Borgia et al. (2010). Fig. 2 shows the two parts of the dump with the complex digitation of intertidal sediments underneath. In our conceptual model (Fig. 3), the fresh recharge-water mixes with the fluids originally contained in the dump materials and percolates downward, displacing the saline fluids contained in the intertidal deposits underneath the dump. We account for reactions among the fluid phases and solid phases of the rock matrix. Although probably present, we do not include density or permeability changes that are a consequence of these reactions.

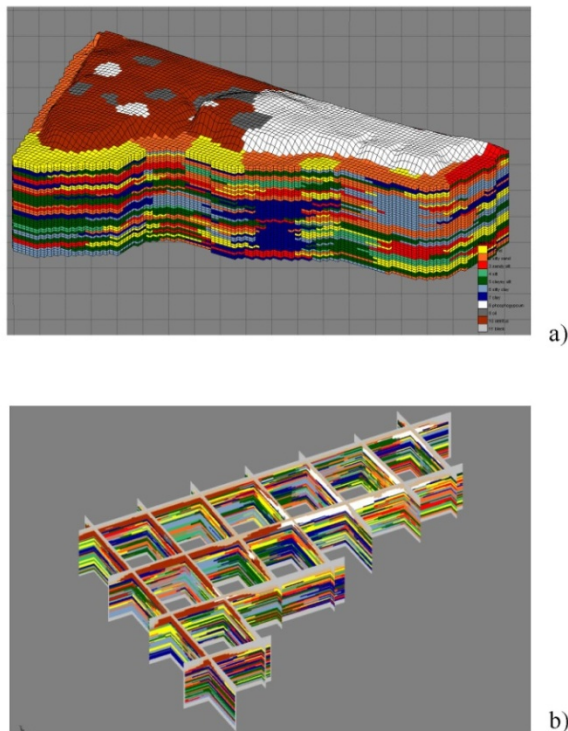


Figure 2. The geologic model after Borgia et al. (2010). Note the complex relations among hydrogeologic units that are reflected in the model. a) 3D view of the modeled dump and underlying barena deposits: white is phosphogypsum, brown is toxic-waste, gray are hydrocarbons. b) Box cross-section of the model.

There are a total of five different fluid compositions to consider (Table 1), in addition to the various mineral phases (Table 2). Since we have not done any laboratory experimental study of the behavior of the system, the goal of our modeling is to investigate possible reaction scenarios among the various fluids and rock phases during downward percolation that could inhibit or enhance the downward migration of pollutants.

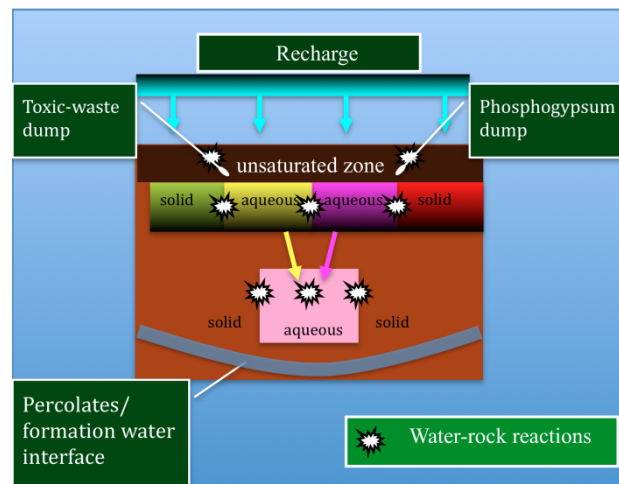


Figure 3. Conceptual model for the reactions occurring in the Passo a Campalto dump system. There are five different water components in addition to the various mineral phases.

TMT2-CODE

To represent the complex topological relationships among the various lithological units of the intertidal deposits of the Venetian Lagoon, we used GMS™ (GMS, 2005) as the geologic graphical user interface to construct (from a conceptual model) a numerical model based on a MODFLOW (MODFLOW, 1996) grid. We then translated this grid to a TOUGH2 grid (Pruess et al., 1999), to be used in TOUGH-REACT (Xu et al., 2005), using the TMT2 code (Borgia et al., 2010; TMT2, 2012). The output files are either read back into GMS or read into other plotting software such as SURFER™ or TECHPLOT™.

MODFLOW specifically requires a rectangular structured grid made of columns, rows, and layers of cells, which are only in part active. In contrast, TOUGH2 and TOUGH-REACT have cells organized in a vector, with active cells only. Each cell in the vector contains the identification code, the volume, the cells to which it is connected and the interface areas, the distances to this area, and angles with the gravity acceleration of the connections. MODFLOW's constant head cells are translated into TOUGH2 as unchanging cells with "infinite" volume. MODFLOW recharge is translated into water-generation cells.

Table 1. The five water types used in the TOUGHREACT model

Chemical species	Phosphogypsum process water	Toxic-waste water	Hydrocarbon- contaminated water	Sediments water	Rain water
H ₂ O	1.000 E+00	1.000 E+00	1.000 E+00	1.000 E+00	1.000 E+00
H ⁺	1.000 E-02	1.000 E-06	0.900 E-06	1.000 E-08	1.000 E-06
Na ⁺	1.400 E-01	1.400 E-04	1.400 E-04	5.760d-1	1.400 E-04
K ⁺	2.623 E-03	1.900 E-05	1.900 E-05	1.260d-2	1.900 E-05
Mg ⁺⁺	7.660 E-03	0.900 E-04	0.900 E-04	6.170d-2	0.900 E-04
Ca ⁺⁺	4.225 E-02	7.700 E-05	7.700 E-05	1.220d-2	7.700 E-05
Al ⁺⁺⁺	2.200 E-05	1.200 E-07	1.200 E-07	5.570d-6	1.200 E-12
Fe ⁺⁺	2.100 E-05	2.100 E-05	2.100 E-06	8.460d-10	2.100 E-20
Fe ⁺⁺⁺	9.400 E-07	9.400 E-07	9.400 E-08	9.400d-7	9.400 E-13
SiO ₂ (aq)	4.400 E-02	9.400 E-12	9.400 E-12	9.400d-6	9.400 E-12
Cl ⁻	4.389 E-02	2.818 E-04	2.818 E-04	6.848d-1	2.818 E-04
F ⁻	3.000 E-02	0.500 E-12	0.500 E-12	8.220d-5	0.500 E-12
HS ⁻	1.430 E-09	1.430 E-07	1.430 E-07	1.430d-40	1.430 E-40
SO ₄ ⁻⁻	6.010 E-02	2.200 E-05	2.200 E-05	1.107d-2	2.200 E-05
HPO ₄ ⁻⁻	5.000 E-02	5.000 E-12	5.000 E-12	7.430d-7	5.000 E-12
HCO ₃ ⁻	1.500 E-03	1.500 E-04	1.500 E-04	1.670d-3	1.500 E-04
H ₂ AsO ₄ ⁻	1.184 E-10	1.184 E-10	1.184 E-10	2.420d-16	1.000 E-28
Cr ⁺⁺⁺	1.572 E-07	1.200 E-07	1.200 E-07	5.576d-13	1.200 E-26
Methane(aq)	1.600 E-40	1.600 E-40	1.600 E-03	1.600d-40	1.600d-03
Benzene(aq)	4.800 E-40	4.800 E-40	4.800 E-06	4.800d-40	4.800d-06

Table 2. The various mineral phases used in the TOUGH-REACT model.

mineral (vol.frac.)	sand	silty sand	sandy silt	silt	clayey silt	silty clay	clay	phospho- gypsum	toxic waste
Calcite	0.5	0.5	0.45	0.3	0.3	0.3			0.9
Dolomite	0.3	0.3	0.25	0.2	0.2	0.2			
Quartz	0.1	0.1	0.05	0.05	0.05	0.05			
Illite	0	0	0.05	0.15	0.15	0.15	0.3		
Smectite-low-Fe-Mg	0	0	0.1	0.2	0.2	0.2	0.6		
Gypsum								0.7	
Fluorapatite								0.05	
Hydroxylapatite								0.2	

In addition to the parameters used in MODFLOW, we provide the parameters that are specific to TOUGH2 (density, thermal conductivity and heat capacity of rock matrix) and to TOUGH-REACT (mineralogy of solid phases, chemistry of liquid phases etc.).

TOUGH-REACT SIMULATIONS

We run TOUGH-REACT with the EOS3 module. This module provides the

thermophysical properties of air and pure water (Pruess et al., 1999). We ignore heat fluxes, considering the system isothermal at 25°C, because recorded temperatures vary only a few degrees seasonally. Our choice of temperature is slightly higher than the maximum recorded temperature (which is 18°C): at higher temperature, chemical reactions tend to occur faster, while there are larger hydraulic

conductivities; the two processes probably tend to compensate for each other.

We set constant head boundaries at sea level in all cells around the model, which reflect the presence of the lagoon all around the dump. Also, the bottom-layer cells are set at the same constant head. When possible, we verified input parameters and results with other numerical codes: MODFLOW for the hydrogeologic transport and PHREEQ (Parkhurst and Appelo, 1999) for the chemical reactions.

We compute our starting condition for the TOUGH2 simulation by letting the model equilibrate at sea level with no recharge. Then, we introduce a recharge of 70 (mm/a), which is calibrated against a recorded piezometric head, and let the model run for many hundreds of years to achieve steady state. The following reactive-transport runs have a maximum time-step interval of 1 day. Results were obtained at 1, 3.16, 10, 31.6, and 100 years from the creation of the dump. The last two output times approximately correspond to the time at which the barriers were built to isolate the dump from its surroundings and to a future forecast at 70 years.

The pH remains practically at the original seawater value at all times below the dump, suggesting that the sediments are very effective at neutralizing the dump percolates.

RESULTS

Our 3D model shows the downward percolation (over time) of the recharge fluids which dilute the toxic-waste and phosphogypsum-dump aqueous phases. As time passes, these percolates downwardly displace the salty seawater that, at the beginning of the simulation, fills the porous medium from sea level downward. The presence of more impermeable layers at depths of 7–10 m on the toxic-waste side of the model tend to inhibit percolation, while the percolates from the phosphogypsum section of the dump do not have such a continuous clayey layer, thus potentially becoming a threat to the superficial groundwater.

Here, we account for some of the relevant results of the reactive transport simulations, showing the evolution of pH and the hydroxyapatite mineral phase. The pH in the phosphogypsum dump slowly becomes neutralized by the recharge water, from the dump's original pH of 2 (Fig. 4). In keeping with field evidence, it is still below 5 after 31.6 years, and it takes many decades to reach values closer to neutral.

As the pH increases above a value of 4.5, hydroxiapatite precipitates in the phosphogypsum of the dump and remains stable during the whole run of the numerical experiment (Fig. 5). Hydroxyapatite continues to precipitate during our numerical experiment in the sediments underneath the dump (Fig. 5) only down to a

Table 3. Hydrodynamic parameters used for the TOUGH2 model.

	Horizontal Hydraulic Conductivity (m/s)	Vertical Hydraulic Conductivity (m/s)	Porosity	Source
Sand	$5,0 \times 10^{-6}$	$5,0 \times 10^{-6}$	0,3	Lefranc Experimental Tests
Silty Sand	$1,0 \times 10^{-6}$	$0,5 \times 10^{-6}$	0,3	Lefranc Experimental Tests
Sandy Silt	$5,0 \times 10^{-7}$	$2,5 \times 10^{-7}$	0,3	Extrapolated
Silt	$1,0 \times 10^{-7}$	$3,3 \times 10^{-8}$	0,3	Extrapolated
Clayey Silt	$5,0 \times 10^{-8}$	$1,67 \times 10^{-8}$	0,3	Extrapolated
Silty Clay	$1,0 \times 10^{-8}$	$2,0 \times 10^{-9}$	0,3	Extrapolated
Clay	$5,0 \times 10^{-9}$	$5,0 \times 10^{-10}$	0,3	Laboratory Tests
Phosphogypsum	$1,0 \times 10^{-6}$	$0,5 \times 10^{-6}$	0,3	C.V.N. Technical Report
Wastes Detritus, Bitumes	$5,0 \times 10^{-6}$	$2,5 \times 10^{-6}$	0,3	Extrapolated

maximum depth of less than 5 m bsl, even after 100 years. These results indicate that the sediments and the formation seawater are effective in inhibiting the downward transport of at least some of the pollutant species present in the dump. However, some metal ions, such as Fe, Mg, and As, tend to be more mobile and can percolate downward to -10 m bsl in less than 100 years.

CONCLUSIONS

Using the GMS™ conceptual-model-oriented graphic user interface (used for the USGS MODFLOW code), we made a 3D model of the highly complex geologic environment that characterizes the intertidal deposits underneath the dump of Passo a Campalto (Venezia). We translated the MODFLOW grid into a TOUGH2 input file, using the TMT2 code. For visualization purposes, the results can be easily translated back to GMS™ or plotted with any adequate graphical software package.

We ran the TOUGH-REACT with the EOS3 equation of state in isothermal mode and attempted to calibrate the simulations using water-table and chemical-monitoring data.

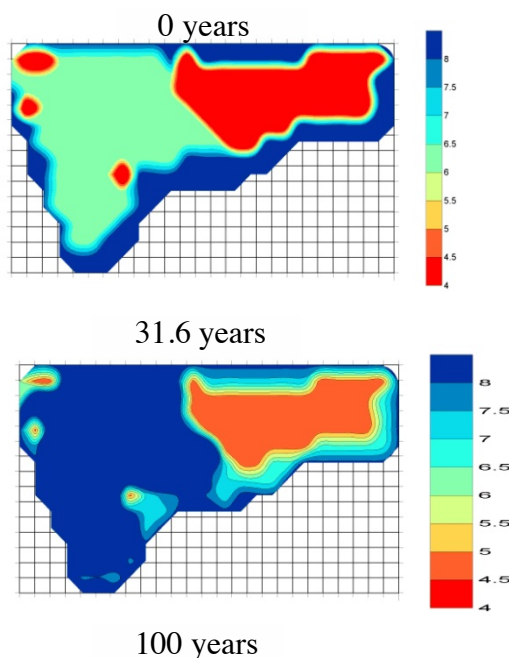


Fig. 4. Evolution of pH in time. Note how the pH of the phosphogypsum dump becomes neutralized by recharge water in more than 100 years.

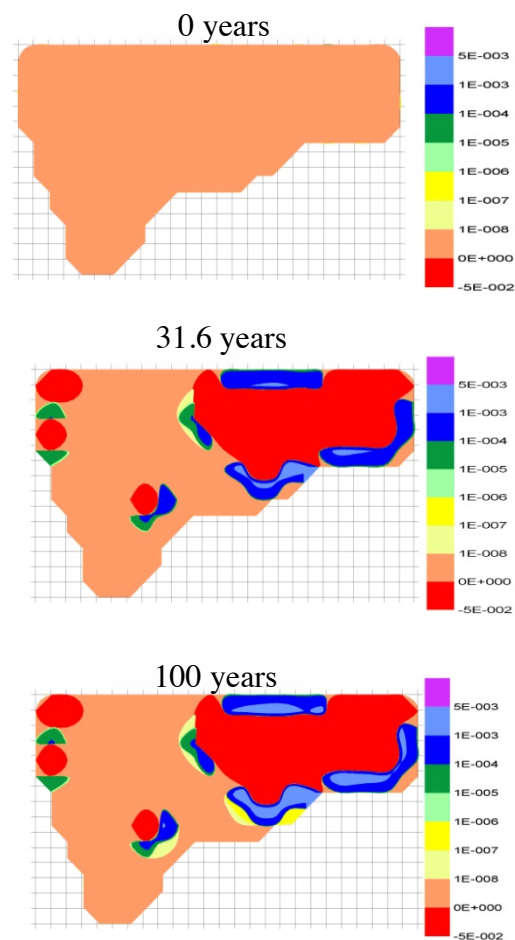


Fig. 5. Evolution of hydroxyapatite mineral phase in time. Note how as the pH of the phosphogypsum dump becomes neutralized the apatite precipitates, becoming immobile, inside the dump.

The results show that while some pollutants are effectively trapped within the dump and the underlying sediments, others have a higher

mobility, leaching downward and potentially polluting the aquifers.

Our simple TMT2 program allows the use of a set of geological graphic user interfaces, available “off the shelf” for MODFLOW with the TOUGH2 series of codes, providing at the same time the freedom to work directly with the TOUGH2 input file.

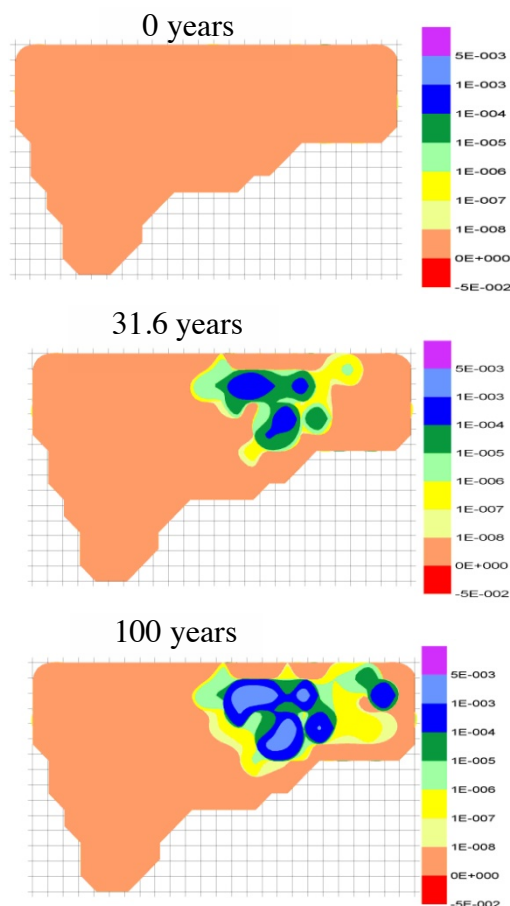


Fig. 6. Evolution of the Hydroxiapatite mineral phase in time at -2 m bsl. Note how, this phase precipitates in the sedimentary layers underneath the dump.

We hope that this effort may enable hydrogeologists concentrating on modeling complex geology (before actually solving the fractured-porous-media flow problem) to use the powerful capabilities inherent in the TOUGH2 codes.

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